

**DEPENDANCE OF PRESSURE INDUCED PHASE  
TRANSITION OF MERCURY CHALCOGENIDES ON  
NEAREST NEIGHBORS' DISTANCE**

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# LIST OF SYMBOLS

$E$	- Total energy
$e$	- Electronic charge
$E_c$	- Correlation energy
$E_F$	- Fermi energy
$E_S$	- Self-potential energy
$E_0$	- Energy of lowest state
$h$	- $h/2\pi$ , where $h$ is Plank's constant
$k$	- Wave vector
$m$	- Rest mass of electron
$m_e^*$	- Effective mass of electron
$P(r)$	- Electronic charge density
$R_a$ $R_b$	- Position vector of nucleus $a$ and $b$
$r_i$	- Position vector of $i$ th electron
$U$	- Internal energy of a lattice
$V(r)$	- Potential energy of an electron in position $r$
$v$	- volume
$Z$	- Valance of the metal
$\alpha$	- $m/m_e^*$
$\psi_i(r)$	- Wave function of electron in position $r$
$\psi_i^*(r)$	- Complex conjugate of $\psi_i(r)$
$E_0$	- Maximum energy state at $0^\circ K$

# ABSTRACT

The relationship between the transition pressure and nearest neighbors' distance for mercury chalcogenides has been investigated. The homopolar energy for both high and low pressure phases has been calculated for different nearest neighbors' distances. Variation of nearest neighbors' distance was achieved by varying the percentage composition,  $x$ , of  $\text{HgSe}_{(1-x)}\text{Te}_x$  alloys. From the computed result it has been found that the transition pressure is a linear function of nearest neighbors' distance.

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## UNITS

It is convenient to use so called atomic units in calculation of total energy of solids. As a unit of length we have taken Bohr radius of Hydrogen  $a_0 = h^2/me^2$  as a unit and designated this as Bohr Unit (B.U.). The unit of energy has been taken as Rydberg (ryd). In cgs units the conversion factors are as follows:

$$\text{One Bohr Unit} = 5.2917 \times 10^{-9} \text{ cm}$$

$$\text{One Rydberg} = 13.6 \text{ electron Volts}$$

Other conversion factors used in calculations are:

$$\text{One electron Volt} = 1.5911 \times 10^{-12} \text{ erg}$$

$$\text{One erg/cm} = 1 \text{ dyne}$$

$$\text{One bar} = 1 \times 10^{-6} \text{ dyne/cm}^2$$



CHAPTER 1

CHAPTER 1

1. INTRODUCTION

Bridgman<sup>[1]</sup> measured the compressibility of HgTe and HgSe at room temperature as a function of hydrostatic pressure up to 50 kbar. He observed sharp changes in compressibility near 13 kbar and 7.5 kbar for HgTe and HgSe respectively. He attributed the change to the solid state polymorphic phase transformation and correctly assumed that the transition represents a change from zinc-blende to hexagonal cinnabar structure. Jayaraman et al<sup>[2]</sup> and Mariano and Warekois<sup>[3]</sup> observed that HgTe phase transformation takes place at 14 kbar. This observation has been made by McCartney<sup>[14]</sup>. Kafalas et al<sup>[5]</sup> confirmed the transition pressure of HgSe to be 8 kbar.

Blair and Smith<sup>[6]</sup> noted that an increase in resistivity by a factor of  $10^4$  and  $10^5$  occurs for HgTe on transition. Kafalas et al observed similar change in HgSe. Pressure, thus, transforms a semimetal with narrow energy-gap to a wide-band-gap semiconductor.

The transition from Zinc-blende to the cinnabar structure, according to McCartney, may be regarded as taking place by the way of slight distortion of the rhombohedra formed by cations, together with the movement of the anions into positions which results in formation of infinite -Te-Hg-Te or -Se-Hg-Se- chains parallel to the c-axis.

It was observed that since there is no structural difference between HgTe and HgSe, the difference in transition pressure must be due to the difference in nearest neighbors' distance. Lombos<sup>[7]</sup> proposed that the transition pressure is a linear function of nearest neighbors' distance for alloys or compounds of similar crystalline structure.

From the data derived from Jacobs<sup>[8]</sup> work it was found that for Rubidium and Potassium halides the assumption is true and the transition pressure is indeed a function of the nearest neighbors' distance.

In this report we shall demonstrate that the assumption is also valid for covalent crystals by showing that for mercury chalcogenides the transition pressure is a function of nearest neighbors' distance. The change in nearest neighbors' distance will be achieved by varying the composition of  $\text{Hg Se}_{1-x} \text{Te}_x$  alloy. We shall vary  $x$  in steps of 0.2 that is in steps of 20%.

## 2. TRANSITION PRESSURE AND ENERGY

When two phases of a crystal are in equilibrium, the thermodynamic potentials of the two phases must be equal, that is,

$$U_1 - TS_1 + PV_1 = U_2 - TS_2 + PV_2 \quad \text{--- (1)}$$

where symbols have their usual thermodynamic meanings and subscript 1 and 2 represent the low and high pressure phases respectively. The internal energy  $U$  can be subdivided into thermal energy and lattice energy. The latter quantity is usually expressed in terms of Coulomb, dipole - dipole, dipole - quadrupole and repulsion energies for ionic crystals and for covalent crystals it is expressed in terms of homopolar energies in addition to ionic energies.

Jacob<sup>[8]</sup> neglected the temperature terms in comparison with the pressure terms and approximated the transition pressure as follows:

$$P = \frac{E_2(r) - E_1(r)}{V_1 - V_2} \quad \text{--- (2)}$$

where  $E_1(r)$  and  $E_2(r)$  are the lattice energies at 0°K and  $V_1$  and  $V_2$  are the molecular volume of the phases.

The mercury chalcogenides are predominantly covalent in character with only minor ionicity. The ionic character of the crystals were calculated by the method outline by Pauling<sup>[9]</sup>. From computation it was found that

for HgSe ionic energy constitutes only about 6% of the lattice energy and for HgTe it is about 1% of the total energy.

The homopolar energy associated with the mercury chalcogenides will be calculated, in the following sections, basically from modified Hartree-Fock energy equation.

## CHAPTER 2

### 1. HOMOPOLAR ENERGY OF A CRYSTALLINE SOLID

The homopolar energy of the mercury chalcogenides is determined by method similar to the physical principles outlined by Wigner and Seitz<sup>[9]</sup> in their classical study. The method is described here as a reference.

The classical Hamiltonian for a "n" particle system can be written as

$$H = - \sum_{i=1}^n \frac{h^2}{2m_i} \nabla^2 + V(x, y, z, \dots, x_n, y_n, z_n) \quad \text{--- (3)}$$

where  $m_i$  = mass of the  $i$ th particle

$\nabla$  = Laplacian operator

$x_i, y_i, z_i$  = Cartesian coordinates

If we consider an atom with nuclear charge  $Ze$  where  $Z$  is the atomic number and  $r_i$  the position vector of the  $i$ th electron, we have,

$$\begin{aligned} V(x, y, z, \dots, x_n, y_n, z_n) &= V(r_1, r_2, \dots, r_n) \\ &= - \sum_{i=1}^N \frac{Ze^2}{r_i} + 1/2 \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{r_{ij}} \end{aligned} \quad \text{--- (4)}$$

Where  $\frac{e^2}{r_{ij}}$  = Coulomb interaction

$\frac{Ze^2}{r_i}$  = potential energy of the  $i$ th electron in the field of nucleus

and  $N = Z$

Rewriting eqn (3)

$$\begin{aligned} H &= - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{i=1}^N V_i(r_i) \\ &= - \sum_{i=1}^N \left[ \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{Ze^2}{r_i} \right] + \sum_{i=1}^N V_i(r_i) \end{aligned} \quad \text{--- (5)}$$

Where  $V_i(r_i)$

$$= 1/2 \sum_{i \neq j}^N \frac{e^2}{r_{ij}}$$

If we ignore the interaction between the wavefunction due to the Hamiltonian  $H$ , and if we have

$$\psi = \psi_1(r) \psi_2(r) \dots \psi_n(r) \quad \text{--- (6)}$$

then equation (3) can be written as

$$\begin{aligned} - \sum_{i=1}^N \left[ \left( \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{Ze^2}{r_i} \right) + V_i(r_i) \right] \psi_1 \psi_2 \dots \psi_n &= E \psi_1 \psi_2 \dots \psi_n \end{aligned} \quad \text{--- (7)}$$

Dividing both sides by  $\psi$ , we have

$$- \sum_{i=1}^N \frac{1}{\psi_i} \left[ \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{Ze^2}{r_i} + V_i(r_i) \right] \psi_i = E \quad \text{--- (8)}$$

which can be separated into  $N$  equations

$$- \left[ \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{Ze^2}{r_i} + V_i(r_i) \right] \psi_i = E_i \psi_i \quad \text{--- (9)}$$

where

$$\sum_{i=1}^N E_i = E$$

We now assume that Schrodinger equation is separable and each electron can be represented by its own wavefunction which in turn is a function of co-ordinates of that electron only. This is known as One Electron Approximation. Hence, the equation which one electron function  $\psi_i(r_i)$  of the  $i$ th electron satisfies is

$$\left[ \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{Ze^2}{r_i} - V_i(r_i) \right] \psi_i = E_i \psi_i \quad \text{-- (10)}$$

Each electron is thus in the field of the nucleus and in the field due to the charge cloud of all the other electrons. Hence, the potential energy of the  $i$ th electron is

$$V_i(r_i) = e^2 \sum_{j \neq i}^N \int |\psi_j(r_j)|^2 / r_{ij} dr_j \quad \text{-- (11)}$$

From equation (10) and (11), we have

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(r_j)|^2}{r_{ij}} dr_j \right] \psi_i(r_i) \\ = E_i \psi_i(r_i) \quad \text{-- (12)} \end{aligned}$$

This is Hartree equation. Although Hartree method gives best ground state wavefunction, it is not the most accurate method of calculating the energy.

In the Hartree solution the electron-electron interaction representing the mutual potential energy of two charge distributions, calculated in the classical way, has been included. However, the possibility of exchange of electrons in which both the orbitals  $i$  and  $j$  enter, has not been taken into consideration.

Fock proposed a method of treating the exchange interaction between the electrons. He showed that once the wavefunction of the core electrons has been obtained by Hartree method, the Schrodinger equation for valance electron could be made to incorporate the exchange energy term by inclusion of exchange integral.

In the following pages we shall develop the Hartree-Fock equation for calculation of binding energy of the mercury chalcogenides.



Let the alloy be composed of  $N$  atoms each with  $Z$  electrons hence there are  $ZN$  electrons each with charge  $-e$  and  $N$  nuclei each with charge  $Ze$ . Then the Hamiltonian operator is

$$H = - \sum_{i=1}^{ZN} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i=1}^{ZN} \sum_{a=1}^N \frac{Ze^2}{|R_a - r_i|} + 1/2 \sum_{i \neq j}^{ZN} \sum_{a=1}^N \frac{e^2}{|r_i - r_j|} + 1/2 \sum_{a \neq b}^N \sum_{a=1}^N \frac{Ze^2}{|R_a - R_b|} \quad (14)$$

where  $r_i$  is the position vector of the  $i$ th electron and  $R_a$  is that of the nucleus  $a$ .

Let  $V_a(r_i)$  be the potential energy of the  $i$ th electron in the field of the ion-core  $a$ , then Hamiltonian operator becomes

$$H = - \sum_{j=1}^{ZN} \frac{\hbar^2}{2m_j} \nabla_j^2 + \sum_{i=1}^{ZN} \sum_{a=1}^N V_a(r_i) + 1/2 \sum_{i \neq j}^{ZN} \sum_{a=1}^N \frac{e^2}{|r_i - r_j|} + 1/2 \sum_{a \neq b}^N \sum_{a=1}^N \frac{Ze^2}{|R_a - R_b|} \quad (15)$$

where  $r_{ij} = |r_i - r_j|$

and  $R_{ab} = |R_a - R_b|$

Let the normalized, antisymmetric total wave function be

$$\Psi = \frac{1}{\sqrt{N!}} \sum_p (-1)^p p \varphi_1(x_1) \varphi_2(x_2) \dots \varphi_n(x_n) \dots \quad (16)$$

$$\text{then } E = \int \psi^* H \psi d\tau = (1/N!) \int \psi^* H \psi d\tau$$

$$= \frac{1}{N!} \sum_p (-1)^p \psi_1(x_1) \psi_2(x_2) \dots \psi_n(x_n) \left[ - \sum_{i=1}^{2N} \frac{\hbar^2}{2m_i} \right]$$

$$\nabla_i^2 + \sum_a \sum_{i=1}^{2N} V_a(r_i)$$

$$+ 1/2 \sum_{i \neq j} \sum_{a=1}^{2N} \frac{e^2}{r_{ij}} \psi_1(x_1) \psi_2(x_2) \dots \psi_n(x_n) + 1/2$$

$$\sum_{a=1}^N \sum_{b=1}^N \frac{Z e^2}{R_{ab}} \dots (17)$$

Because of orthogonality and normalization of  $\psi_i$ , the expression becomes

$$E = \sum_i \psi_i^*(x_i) \left[ - \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_a V_a(r_i) \right] \psi_i(x_i) dx_i$$

$$+ 1/2 \sum_{i \neq j} \sum_{a=1}^N \iint \left[ \psi_i^*(x_i) \psi_j^*(x_j) - \psi_i(x_j) \psi_j(x_i) \right] \frac{e^2}{r_{ij}} \psi_i(x_i) \psi_j(x_j) dx_i dx_j$$

$$+ 1/2 \sum_{a \neq b} \sum_{i=1}^N \sum_{j=1}^N \frac{Z e^2}{R_{ab}} \dots (18)$$

Equation (18) can be written as

$$E = \sum_i \int \psi_i^*(x_i) \left[ - \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_a V_a(r_i) \right] \psi_i(x_i) dx_i$$

$$+ 1/2 \sum_{i=1}^N \sum_{j=1}^N \iint \frac{e^2}{r_{ij}} |\psi_i(x_i)|^2 |\psi_j(x_j)|^2 dx_i dx_j$$

$$-1/2 \sum_{i \neq j}^N \sum_{j=1}^N \iint \frac{e^2}{r_{ij}} \psi_i^*(x_j) \psi_j^*(x_i) \psi_i(x_i) \psi_j(x_j) dx_i dx_j + 1/2$$

$$\sum_{a=b}^N \sum_{ab} \frac{Nze^2}{R_{ab}}$$

-- (19)

The second term is Coulomb interaction energy and the third term is exchange energy.

The summation over the spin variable for the first two converts  $\psi_i$  to  $\psi_i$  and  $x_i$  to  $r_i$ .

If  $\psi_i$  and  $\psi_j$  have the same spin, the exchange energy term becomes

$$\frac{1}{2} \iint \frac{e^2}{r_{ij}} \psi_i^*(r_j) \psi_j^*(r_i) \psi_i(r_i) \psi_j(r_j) dr_i dr_j \quad \text{-- (20)}$$

If, on the other hand,  $\psi_i$  and  $\psi_j$  have opposite spin then the integral becomes zero. The exchange term is, therefore,

$$-1/2 \sum_{i \neq j}^N \sum_{j=1}^N \iint \frac{e^2}{r_{ij}} \psi_i^*(r_j) \psi_j^*(r_i) \psi_i(r_i) \psi_j(r_j) dr_i dr_j$$

-- (21)

Since the value of a definite integral is independent of the symbols used, for the variable of integration we can use  $r_1$  and  $r_2$  instead of  $r_i$  and  $r_j$  and  $r_{12}$  instead of  $r_{ij}$ , giving

$$E = \sum_i^N \int \psi_i^*(r_i) \left[ -\frac{h^2}{2m_i} \nabla_i^2 + \sum_a^N \frac{v_a}{r_{ia}} \right] \psi_i(r_i) dr_i$$

$$\begin{aligned}
 & + \sum_{i \neq j}^N \sum_{j}^N \iint \frac{e^2}{R_{12}} |\psi_i(r_1)|^2 |\psi_j(r_2)|^2 dr_1 dr_2 \\
 & - \sum_i^N \sum_j^N \iint \frac{e^2}{r_{12}} \psi_i^*(r_2) \psi_j^*(r_1) \psi_i(r_1) \psi_j(r_2) dr_1 dr_2 \\
 & + 1/2 \sum_{a \neq b}^N \sum_{b}^N \frac{e^2}{R_{ab}}
 \end{aligned} \quad (22)$$

For one electron approximation

$$\begin{aligned}
 E_i = & \int \psi_i^*(r_1) \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_a^N V_a(r_1) \right] \psi_i(r_1) dr_1 \\
 & + \sum_j^N \iint \frac{e^2}{R_{12}} |\psi_i(r_1)|^2 |\psi_j(r_2)|^2 dr_1 dr_2 \\
 & - \sum_j^N \iint \frac{e^2}{r_{12}} \psi_i^*(r_1) \psi_j^*(r_2) \psi_i(r_2) \psi_j(r_1) dr_1 dr_2
 \end{aligned} \quad (23)$$

The factor 1/2 disappears because the number i occurs in both of the double summations

Hartree - Fock equation can be written as

$$\begin{aligned}
 & \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_a^N V_a(r_1) + e^2 \sum_j^N \int \frac{|\psi_j(r_2)|^2}{r_{12}} dr_2 \right] \psi_i(r_1) \\
 & - e^2 \sum_j^N \frac{\int \psi_j^*(r_2) \psi_i(r_1) \psi_j(r_2) dr_2}{r_{12} \psi_i(r_1)} \psi_i(r_1) = E \psi_i(r_1)
 \end{aligned} \quad (24)$$

$$\text{Let } \psi_k(r) = \frac{1}{\sqrt{V}} e^{i k r} \quad (25)$$

where V is the volume, be eigenfunction of the equation (24).

Let the subscript k and k' distinguish between the eigenfunctions rather than r<sub>i</sub> and r<sub>j</sub>. Then the equation (24) becomes.

$$\frac{\hbar^2}{2m} \nabla^2 \psi(r_1) - e^2 \sum_{k'} \left[ \frac{\int \psi_{k'}(r_2) \psi_k(r_2) \psi_k(r_1) dr_2}{r_{12} \psi_k(r_1)} \right] = E(k) \psi_k(r_1) \quad (26)$$

Using equation (25) the second term of equation (26) becomes

$$- \frac{e^2}{V} \sum_{k'} \left[ \int \frac{e^{i(k-k') \cdot (r_2 - r_1)}}{r_{12}} dr_2 \right] \psi_k(r_1) \quad (27)$$

The integral may be written as

$$e^{-i(k-k')r_1} \int \frac{e^{i(k-k')r_2}}{r_{12}} dr_2 \quad (28)$$

Suppose that  $\phi(r)$  is the potential at  $r$  due to the distribution of charge whose density is given by the function  $e^{i(k-k')r}$ . Then  $\phi(r)$  must satisfy

$$\nabla^2 \phi(r) = -4\pi e^{i(k-k')r} \quad (29)$$

The solution of this equation is

$$\phi(r) = \frac{4\pi e^{i(k-k')r}}{|k-k'|^2} \quad (30)$$

The potential at the point  $r_1$  is

$$\phi(r_1) = \int \frac{e^{i(k-k')r_2}}{r_{12}} dr_2 \quad (31)$$

This must be equal to

$$4\pi e^{i(k-k')r_1} / |k-k'|^2 \quad (32)$$

Therefore,

$$\frac{e^2}{V} \sum_{k'} \int \frac{e^{i(k-k')(r_2-r_1)}}{r_{12}} dr_2 = E_x(k) \psi_k(r) \quad (33)$$

$$\text{and } E_x(k) = - \frac{4\pi e^2}{V} \sum_{k'} \frac{1}{|K-K'|^2} \quad (34)$$

where

$E_x(k)$  is the exchange energy associated with state  $k$ .  $\psi_k$  is therefore the eigenfunction of Hartree - Fock equation.

To evaluate  $E_x(k)$  given that the volume element  $dk$  of  $k$ -space contains  $v dk/8\pi^3$  orbital state, we have

$$E_x(k) = - \frac{4\pi e^2}{V} \cdot \frac{v}{8\pi^3} \int \frac{dk'}{|K-K'|^2} \quad (35)$$

The integral is taken throughout the Fermi sphere.

$$\begin{aligned} E_x(k) &= - \frac{e^2}{2\pi} \int_0^{K_0} dk' \int_{-1}^1 \frac{k' (d \cos \theta)}{k^2 + k'^2 - 2kk' \cos \theta} \quad (36) \\ &= - \frac{e^2}{2} \int_0^{K_0} dk' \int_0^1 d\theta \int_0^{2\pi} \frac{k' \sin \theta}{|K-K'|^2} \end{aligned}$$

For the  $k=k'$  the integral is infinite. Therefore, for  $k < k_0$  and  $k > k_0$ , we have

$$E_x(k) = - \frac{e^2 k_0}{2\pi} \left[ 2 + \frac{k_0^2 - K^2}{K_0 K} \ln \left| \frac{K_0 + K}{K_0 - K} \right| \right] \quad (37)$$

Hence

$$E(k) = \frac{\hbar^2 k^2}{2m} - \frac{e^2 K_0}{2\pi} \left[ 2 + \frac{K_0^2 - K^2}{K_0 K} \ln \left| \frac{K_0 + K}{K_0 - K} \right| \right] \quad (38)$$

The total exchange energy per particle of the system is found by integrating the equation (37) over all  $k$ .

Rewriting the equation (19) in  $k$ -space, and noting that at absolute zero there are two electrons with opposite spins in each occupied orbital state, a sum of  $k$  being a sum over all the orbital states, the equation must be multiplied by two.

Hence we have,

$$\begin{aligned}
 NE_0 = & 2 \sum_k \psi_k^*(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_a^N V_a(r) \right] \psi_k(r) dr \\
 & + 2 \sum_k \sum_{k'} \iint \frac{e^2}{r_{12}} |\psi_k(r_1)|^2 |\psi_{k'}(r_2)|^2 dr_1 dr_2 \\
 & - \sum_k \sum_{k'} \iint \frac{e^2}{r_{12}} \psi_k^*(r_1) \psi_{k'}^*(r_2) \psi_k(r_2) \psi_{k'}(r_1) dr_1 dr_2 \\
 & + 1/2 \sum_a^N \sum_{B \neq a}^N \frac{e^2}{R_{ab}}
 \end{aligned} \quad \text{--- (39)}$$

where  $E_0$  is the average energy per electron,

Let  $V_a(r)$  be the potential energy of an electron in the field of the ion-core whose nucleus has position vector  $R_a$ ; we call the cell containing this ion-core as cell 'a'. Then

$$V_a(r) = \sum_a^N V_a(r) \quad \text{--- (40)}$$

$$\begin{aligned}
 U_a(r) &= V_a(r) && \text{within the cell)} \\
 &= 0 && \text{outside the cell)}
 \end{aligned} \quad \text{--- (41)}$$

$V_a(r)$  is symmetrical about the lattice point  $R_a$

$$V_a(r) = V(|r - R_a|) \quad -- (42)$$

Electron density  $P(r)$  for both types of spin at point  $r$  is

$$P(r) = 2 \sum_k |y_k(r)|^2 \quad -- (43)$$

where  $y_k$ 's are normalized.

Now, the first term of the equation (39) is

$$\begin{aligned} & 2 \sum_k \int y_k^*(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_a^N V_a(r) \right] y_k(r) dr \\ &= 2 \sum_k \int y_k^*(r) [E(k) - V(r) + \sum_a^N V_a(r)] y_k(r) dr \\ &= 2 \sum_k E(k) + \sum_a^N \int P(r) [V_a(r) - U_a(r)] dr \\ &= 2 \sum_k E(k) + \sum_a^N \left[ \int P(r) [V_a(r) - U_a(r)] dr \right. \\ & \quad \left. + \sum_{a' \neq a}^N \int_b P(r) [V_{a'}(r) - U_{a'}(r)] dr \right] \quad -- (44) \end{aligned}$$

From definition  $V_a(r) - U_a(r)$  is zero within cell 'a' and

$U_a(r)$  is zero within any other cell 'b'. Therefore, equation (44) becomes

$$2 \sum_k E(k) + \sum_a^N \sum_{a' \neq a}^N \int_b P(r) V_{a'}(r) dr \quad -- (45)$$

Let us assume -(1) that outside the cell 'a'

$$V_a(r) = -\frac{e^2}{r - R_a} \quad -- (46)$$



(2) that distribution of charge within any cell 'a' is spherically symmetrical, i.e. for points outside cell 'a' the charge can be regarded as being concentrated at center.

$$\int_b P(r) V_a(r) dr = - \int_b \frac{e^2}{|r-R_a|} P(r) dr = - \frac{e^2}{R_{ab}} \quad (47)$$

The Coulombs' term (second term) in equation (39) is

$$\begin{aligned} & 1/2 \iint \frac{e^2}{r_{12}} P(r_1) P(r_2) dr_1 dr_2 = 1/2 \sum_a^N \sum_b^N \int_a \int_b \frac{e^2}{r_{12}} \\ & P(r_1) P(r_2) dr_1 dr_2 + \frac{N}{2} \int_a \int_b \frac{e^2}{r_{12}} P(r_1) P(r_2) dr_1 dr_2 \\ & = 1/2 \sum_a^N \sum_{a \neq b}^N \frac{e^2}{R_{ab}} + \frac{N}{2} \int_a \int_b \frac{e^2}{r_{12}} P(r_1) P(r_2) dr_1 dr_2 \end{aligned} \quad (48)$$

Then the equation (39) becomes

$$\begin{aligned} NE_0 &= 2 \sum_k E(k) + \frac{N}{2} \int_a \int_b \frac{e^2}{r_{12}} P(r_1) P(r_2) dr_1 dr_2 \\ &= \sum_K \sum_K \iint \frac{e^2}{r_{12}} \psi_k^*(r_1) \psi_k(r_2) \psi_k(r_2) \psi_k^*(r_1) dr_1 dr_2 \end{aligned} \quad (49)$$

Now,

$$2 \sum_k E(k) = N \left( E_0 + \frac{\hbar^2 k^2}{2m} \right) \quad (50)$$

where

$$\alpha = m/m^*$$

(Rest electron mass  
Effective electron mass)

$E_0$  = Energy of the lowest state

$$\frac{\hbar^2 k^2}{2m} = \text{Fermi energy}$$

$$= E_F$$

For a metal of valency  $Z$ , it can be shown (section 6) that the Fermi energy is given by

$$E_F = \frac{2.21 Z^{2/3}}{r_s} \text{ ryd} \quad \text{-- (50) - a}$$

Similarly, the Coulombs' term can be shown to be (Section 9)

$$E_s = \frac{1.2 Z}{r_s} \text{ ryd} \quad \text{-- (51)}$$

The exchange energy term is given by (section 8),

$$E_x = -\frac{0.916Z^{1/3}}{r_s} \text{ ryd} \quad \text{-- (52)}$$

The correlation energy term is given by (section 7),

$$E_c = -\frac{0.876Z^{1/3}}{r_s} + \frac{2.65Z^{1/2}}{r_s^{3/2}} - \frac{0.73Z^{2/3}}{r_s^2} \text{ ryd} \quad \text{-- (53)}$$

Therefore the total energy (homopolar) of a solid of valency  $Z$  is given by

$$E(r_s) = E_0(r_s) + \frac{2.21Z^{2/3}}{r_s} + \frac{1.2Z^{1/2}}{r_s} - \frac{0.916Z^{1/3}}{r_s} - \frac{0.876Z^{1/3}}{r_s} + \frac{2.65Z^{1/2}}{r_s^{3/2}} - \frac{0.73Z^{2/3}}{r_s^2} \quad \text{-- (54)}$$

## 2. INTERATOMIC DISTANCE AND ATOMIC RADII

Interatomic distances for both HgSe and HgTe were calculated by method outlined by Pauling<sup>[9]</sup>, that iterates that bond distance A - B is equal to the arithmetic mean of the distances A - A and B - B. From table 23-1 of reference <sup>[9]</sup> covalent radii for the solids under consideration are

Hg -- 1.48 Å

Se -- 1.14 Å

Te -- 1.32 Å

Therefore, the interatomic distances are

HgSe -- 2.62 Å

HgTe -- 2.80 Å

For the alloys  $\text{HgSe}_{1-x}\text{Te}_x$  the interatomic distance is assumed to be a linear function of  $x$ , the percentage composition and is shown in fig. 1.

For calculation of homopolar energy the atomic radii,  $r_s$ , have been assumed such that the interatomic distance between like neighbors is equal to twice the atomic radii of the alloys.

It has also been assumed that change from zinc-blende to Cinnabar structure changes the interatomic distances by -4%. [Ref. 11].

### 3 LOWEST ENERGY STATE

The wavefunction  $\psi_0$  and the energy  $E_0$  of the lowest state may be found by integrating the Schrodinger equation

$$\frac{d^2\psi_0}{dr^2} + \frac{2}{r} \frac{d\psi_0}{dr} + \frac{2m}{r} [E_0 - V(r)] \psi_0 = 0 \quad (55)$$

within an atomic sphere. The radius of this sphere is,  $r_s$ , the atomic radius, defined by

$$\frac{4\pi}{3} r_s^3 = \frac{N}{V} \quad (56)$$

where  $v$  is the volume and  $N$  is the number of atoms. The boundary condition to be satisfied by this equation is that the normal derivative of  $\psi_0$ , which is assumed to be spherically symmetrical within the atomic sphere, vanishes at the surface, that is,

$$\left( \frac{d\psi}{dr} \right)_{r=r_s} = 0 \quad (57)$$

The function  $V(r)$  used by Wigner and Seitz for Sodium was a semi-empirical function constructed from spectroscopic transition by Prokofiev<sup>[12]</sup>. Quantum Defect method is most accurate but requires also spectroscopic data. Since no relevant data are available for mercury chalcogenides empirical method has been used.

The empirical method suggested by Gruneisen<sup>[13]</sup> and modified by Bardeen<sup>[14]</sup> and Frohlich<sup>[15]</sup> requires definite

experimental data. Since energy values for at least three values of  $r_g$  are required for solution of Bardeen's equation, empirical method outlined by Bardeen was not used.

From the published data for Lithium, Sodium and other alkali metals it was found that the lowest state energy  $E$ , is proportional to Fermi energy and is related to the atomic radius and  $\psi_0(r)$ . That is,

$$E_0(r_g) = k E_F \quad \text{-- (58)}$$

The factor  $k$  varies between 0.795 to 0.87 for alkali metals.

In our calculations  $k$  has been assumed to be 0.95. The reason for the higher value of the proportionality factor  $k$  are - that the alloys under consideration are divalent and that value of  $k$  is assumed to be related to  $r_g$  and  $r_s$  for the alloys under consideration is much smaller than the alkali metals mentioned above.

It should be noted that  $k$  acts as a scaling factor in determination of transition pressure and has no effect on the transition pressure-interatomic distance relationship.

#### 4. FERMI ENERGY

Let the density of states in energy  $N(E)$  be defined as the number of the orbital states with energies lying between  $E$  and  $dE$ .

Therefore, number of orbital states  $V(E)$  with energies less than  $E$  is

$$V(E) = \int_0^E N(E) dE \quad \text{--- (59)}$$

Each orbital stage can be represented by a triad in rectangular coordinate system, positive integral values of  $n_x, n_y, n_z$ . It can be shown that

$$V(E) = \frac{1}{8} \left[ \frac{4}{3} \pi \left( \frac{2mL^2}{h^2} E \right)^{3/2} \right] = \frac{V}{6\pi^2} \left( \frac{2m}{h^2} \right)^{3/2} (E)^{3/2} \quad \text{--- (60)}$$

where  $v = L^3$ . Differentiating with respect to  $E$ , the density of state is

$$N(E) = \frac{V}{4\pi^2} \left( \frac{2m}{h^2} \right)^{3/2} E^{1/2} \quad \text{--- (61)}$$

If  $N$  is the total number of electrons, we have

$$N = 2 \int_0^{\xi_0} N(E) dE = \frac{V}{2\pi^2} \left( \frac{2m}{h^2} \right)^{3/2} \frac{2}{3} \xi_0^{3/2} \quad \text{--- (62)}$$

where  $\xi_0$  is the maximum energy state at absolute zero. The above equation gives

$$\xi_0 = \left( \frac{2m}{h^2} \right)^{-1} \left( \frac{3\pi^2}{V} N \right)^{2/3} \quad \text{--- (63)}$$

The average kinetic energy per electron, called Fermi energy is given by

$$E_F = \kappa \frac{3}{5} \zeta \quad \text{-- (64)}$$

for a monovalent solid the atomic radius  $r_s$  is given by

$$\frac{V}{N} = \frac{4\pi}{3} r_s^3 \quad \text{-- (65)}$$

Therefore,

$$\zeta = \frac{h^2}{2m} \left( \frac{9}{4} \pi \right)^{2/3} \frac{1}{r_s^2} \quad \text{-- (66)}$$

and

$$E_F = \frac{3}{5} \frac{h^2}{2m} \left( \frac{9}{4} \pi \right)^{2/3} \frac{1}{r_s^2} \text{ electron volts} \quad \text{-- (67)}$$

$$\begin{aligned} \text{In Rydbergs} \quad E_F &= \frac{3}{5} \frac{h^2}{2m} \left( \frac{9}{4} \pi \right)^{2/3} \frac{1}{r_s^2} \circ \left( \frac{me^2}{h^2} \right)^2 \left( \frac{2h^2}{me^4} \right) \\ &= \frac{3}{5} \left( \frac{9}{4} \pi \right)^{2/3} \frac{1}{r_s^2} = \frac{2.21}{r_s^2} \quad \text{-- (68)} \end{aligned}$$

For polyvalent metals the atomic radius  $r_s$  is replaced by  $(Z^{1/3} r_s)$ , which gives

$$E_F = \frac{2.21 Z^{2/3}}{r_s^2} \text{ ryd} \quad \text{-- (69)}$$

## 5. CORRELATION ENERGY

To treat interaction more accurately than permitted by Hartree - Fock approximation, Wigner [16] obtained "correlation energy"

$$E_c = \frac{0.88}{r_s + 7.79} \text{ ryd} \quad \text{--- (70)}$$

Wigner arrived at the formula by interpolation of correlation energies for small and large  $r_s$ .

Gell-Mann and Bruckner [17] found that

for  $r_s < 1$

$$E_c = 0.0622 \ln r_s - 0.096 \text{ ryd} \quad \text{--- (71)}$$

The calculation of the energy of lattice has been improved (Coldwell-Horsfall and Maradudin 1960; Carr et al 1961) by inclusion of zero point motion and of anharmonic interaction. Therefore, for monovalent metal

$$E_c = - \frac{0.876}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} \quad \text{--- (72)}$$

For polyvalent metals we replace  $r_s$  by  $r_s^{1/3}$

which gives

$$E_c = - \frac{0.876Z^{1/3}}{r_s} + \frac{2.65Z^{1/2}}{r_s^{3/2}} - \frac{0.73Z^{2/3}}{r_s^2} \quad \text{--- (73)}$$

For  $\text{HgSe}_{1-x}\text{Te}_x$  alloys  $Z = 2$ , which gives



$$E_c = \frac{1.103716}{r_s} + \frac{3.74776}{r_s^{3/2}} - \frac{1.158853}{r_s^2} \quad (74)$$

Let the primed figures denote the high pressure values,  
then

$$\Delta E_c = E_c' - E_c \quad (75)$$

## 6. EXCHANGE ENERGY

The total exchange energy is found by integrating equation (37) over the Fermi sphere. Thus

$$\begin{aligned}
 \sum_k E_x(k) &= - \frac{e^2}{2\pi} \sum_k \left[ 2K_0 + \frac{K_0^2 - K^2}{KK_0} \ln \frac{(K_0 + K)}{K_0 - K} \right] \\
 &= - \frac{e^2}{2\pi} \frac{V}{8\pi} \int_0^{K_0} \left[ 2K_0 + \frac{K_0^2 - K^2}{KK_0} \ln \frac{(K_0 + K)}{K_0 - K} \right] 4\pi K^2 dk \\
 &= \frac{e^2 V}{4\pi^3} K_0^4 = - \frac{e^2 V}{4\pi^3} \left[ \frac{3\pi^2 N}{V} \right]^{4/3} \\
 &= \frac{3e^2 N}{4} \left[ \frac{9}{4\pi^2} \right]^{1/3} \frac{1}{r_s} \quad \text{--- (76)}
 \end{aligned}$$

Where N is the total number of electrons. Thus average exchange energy per electron is

$$E_x = - \frac{3e^2}{4} \left[ \frac{9}{4\pi^2} \right]^{1/3} \frac{1}{r_s} \quad \text{--- (77)}$$

expressing the energy in Rydbergs

$$\begin{aligned}
 E_x &= - \frac{3e^2}{4} \left[ \frac{9}{4\pi^2} \right]^{1/3} \frac{1}{r_s} \left[ \frac{me^2}{h^2} \right] \left[ \frac{2h^2}{me^4} \right] \\
 &= - \frac{0.916}{r_s} \text{ ryd} \quad \text{--- (78)}
 \end{aligned}$$

For polyvalent alloys the exchange energy is

$$E_x = - \frac{0.916}{r_s} \frac{1}{3} \text{ ryd} \quad \text{--- (79)}$$

## 7. SELF -POTENTIAL ENERGY

From equation (48) self-potential energy or the Coulombic term for one electron is

$$E_s = 1/2 \iint \frac{e^2}{r_{12}} P(r_1) P(r_2) dr_1 dr_2 \quad \text{-- (80)}$$

In free electron approximation

$$P(r) = \frac{N}{V} = \frac{3}{4\pi} r_s^3 \quad \text{-- (81)}$$

Therefore, 
$$E_s = \frac{9e^2}{2(4\pi r_s^3)^2} \iint \frac{dr_1 dr_2}{r_{12}} \quad \text{-- (82)}$$

It can be shown [18] that

$$\iint \frac{dr_1 dr_2}{r_{12}} = 32 \pi^2 \frac{r_s^5}{15} \quad \text{-- (83)}$$

Therefore 
$$E_s = \frac{9e^2}{2(4\pi r_s^3)^2} \frac{32 \pi^2}{15} r_s^5 = \frac{3}{5} \frac{e^2}{r_s} \quad \text{-- (84)}$$

Expressing the energy in Rydbergs

$$\begin{aligned} E_s &= \frac{3}{5} \frac{e^2}{r_s} \left[ \frac{me^2}{h^2} \right] \left[ \frac{2h^2}{me^4} \right] \\ &= \frac{1.2}{r_s} \text{ ryd} \quad \text{-- (85)} \end{aligned}$$

For polyvalent alloys and self-potential energy is

$$E_s = \frac{1.2}{r_s} z^{1/3} \text{ ryd} \quad \text{-- (86)}$$


### 8. ELECTRON EFFECTIVE MASS

The value of the electron effective mass  $m_e^*$  of 0.04m for HgSe and 0.03m for HgTe were obtained from Seebeck and Hall coefficient measurements by Harman and Rodots.[19] When the energy gap  $E_g$  at  $k=0$  is smaller than the spin-orbit splitting energy at  $k=0$ , the effective mass is much less than free electron mass. To date no values for spin-orbit splitting energy at  $k=0$  for cinnabar structure of either HgTe or HgSe is known though the energy gap  $E_g$  is assumed to be 2 - 2.3 eV.

In our calculations we have assumed that the change of effective mass at transition is negligible.

R. Piotrkowi and S. Porowski [20] noted that for low pressure HgTe has the semi-metal model (Fig. 6), which has a low effective mass. When the pressure is above transition pressure the band structure changes to Kane model.

According to Piotrkowski  $m_e^*$  in the semi-metal models is independant of pressure and thermo electric power remains constant due to the fact that the slight increase of effective electronic mass is neutralized by decrease in carrier concentration. Experimentally the conductivity is almost constant up to the transmit pressure. The effective mass increases only after the transition has taken place.



We therefore conclude that up to the transition pressure the effective electronic mass remains constant.

## 9. IONIC CHARACTERISTIC

Ionic character of a bond is dependent on the difference of electronegativity of elements forming the bond. The electronegativity of the elements under consideration are as follows<sup>[9]</sup>:

Hg - 1.9

Te - 2.1

Se - 2.4

Ionic character is given by  $1 - e^{-\frac{1}{4} \cdot (x_a - x_b)^2}$

(Ref. 9). For HgSe  $x_a - x_b = 0.5$  and amount of ionic characteristic is 6%. For HgTe  $x_a - x_b = 0.2$  and the amount of ionic characteristic is only 1%.

### CHAPTER 3

#### 1. CALCULATION

The transition pressure for various alloy compositions were calculated by utilizing the equations developed in the previous sections. The nearest neighbors' distance was varied as mentioned previously by changing the composition  $x$  in the family of alloys of type  $\text{HgSe}_{1-x}\text{Te}_x$ .

In calculation, the change in molecular volume at the transition pressure is assumed to be 8% for  $\text{HgTe}$  and 9% for  $\text{HgSe}$ . The volume change for  $\text{HgSe}_{1-x}\text{Te}_x$  alloys is assumed to be linearly proportional to the composition  $x$ .

The molecular volume of  $\text{HgSe}_{1-x}\text{Te}_x$  alloys is as follows:

Composition $x$	0	0.2	0.4	0.6	0.8	1.0
Molecular vol. $\text{cm} \times 10^{-24}$	55.93	58.13	60.39	62.70	65.07	67.50

Molecular volume has been calculated by Ghiacopolos in his Master (1973) [11] thesis. The data shown above have been obtained from his work.

TABLE 1

Low Pressure Phase

HOMOPOLAR ENERGY OF  $HgSe_{1-x}Te_x$  ALLOYS

$x$	Atomic Radius $r_s$ cm	Atomic Radius $r_s$ Bohr Unit	Fermi Energy $E_F$ Rydberg Equation (69)	Energy of Lowest State $E_o$ Rydberg Equation (58)	Energy of Interaction $E_{IS}$ Rydberg Equation (5c)	Exchange Energy $E_{EX}$ Rydberg Equation (75)	Correlation Energy $E_{EC}$ Rydberg Equation (74)
0	1.315	2.4849	14.20441	13.4942	0.96583	0.46445	1.1147
20	1.332	2.5170	14.57299	13.8443	0.95352	0.45853	1.0901
40	1.349	2.5491	14.99768	14.2478	0.94151	0.45275	1.0700
60	1.365	2.5794	15.50900	14.7343	0.93045	0.44744	1.0514
80	1.384	2.6134	16.05281	15.2502	0.91834	0.44161	1.0308
100	1.4	2.6455	16.70937	15.8739	0.90720	0.43626	1.0116

High Pressure Phase

0	1.262	2.3855	15.41279	14.6421	1.00608	0.48380	1.1812
20	1.279	2.4163	15.87301	15.0224	0.99325	0.47764	1.1592
40	1.295	2.4471	16.27424	15.461	0.98075	0.47163	1.1377
60	1.31	2.4762	16.82884	15.9874	0.96922	0.46608	1.1176
80	1.328	2.5089	17.41759	16.5467	0.95659	0.46001	1.0959
100	1.344	2.5397	18.13083	17.2243	0.94499	0.45443	1.0756



ENERGY VARIATION DUE TO POLYMORPHIC  
PHASE TRANSITION

TABLE 2

Percentage Composition -	$\Delta E_F$ Rydberg	$\Delta E_o$ Rydberg	$\Delta E_s$ Rydberg	$\Delta E_c$ Rydberg	$\Delta E_x$ Rydberg
0	1.20838	1.1479	0.04025	0.0665	0.01935
20	1.24002	1.1781	0.03973	0.0691	0.01911
40	1.27656	1.2132	0.03924	0.0677	0.01888
60	1.31984	1.2531	0.03877	0.0662	0.01864
80	1.36478	1.2965	0.03825	0.0651	0.01840
100	1.42146	1.3504	0.03779	0.0640	0.01817

TABLE 3  
VARIATION OF TRANSITION PRESSURE  
WITH ALLOY COMPOSITION

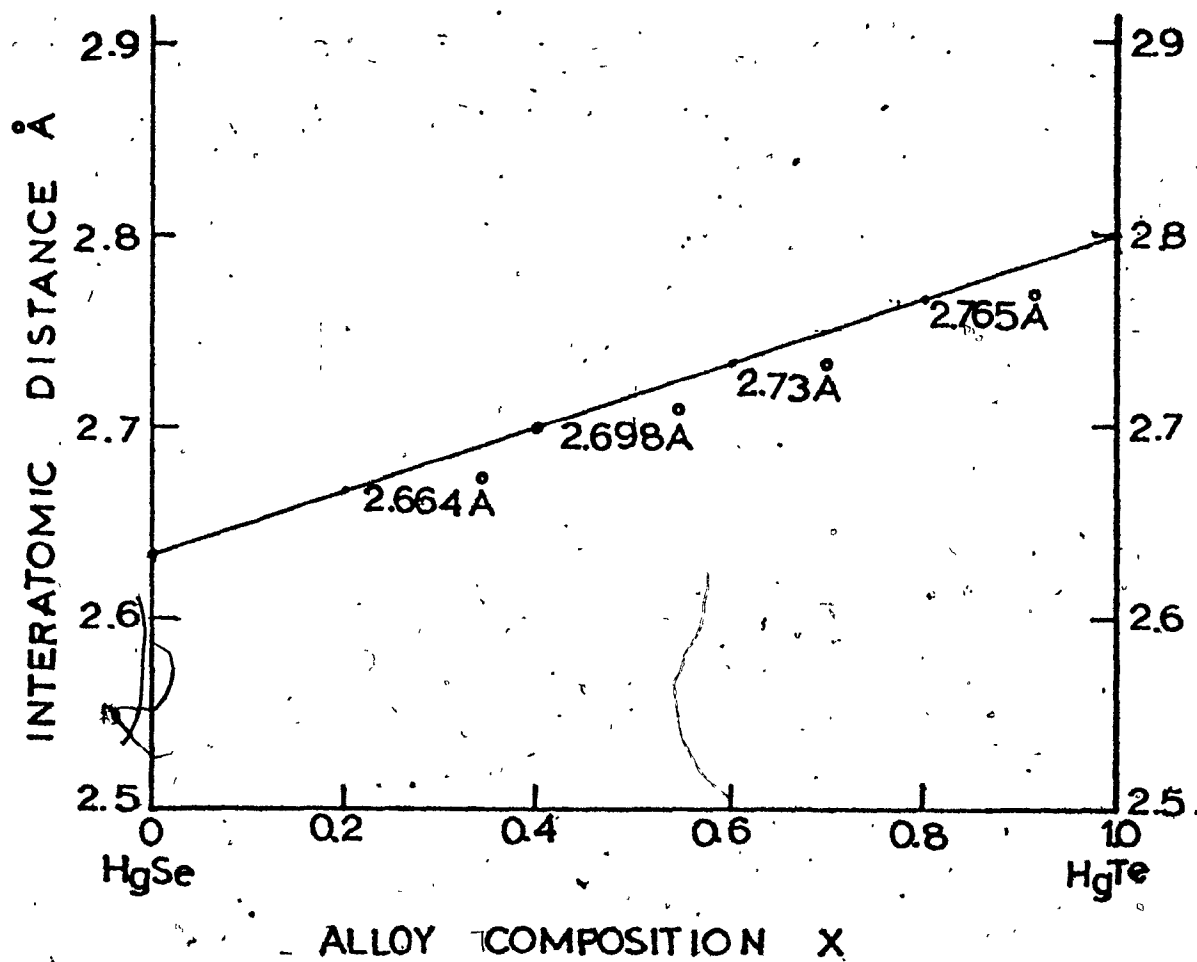
Percentage Composition	$E_2(r) - E_2(r) = E$ Rydberg Equation (2)	E Electron Volts	$E$ ERG $\times 10^{-12}$	$V_1 - V_2 = V$ cm $\times 10^{-24}$	Transition Pressure K Bars Equation (1)
0	0.01235	0.1678	0.26702	5.0337	53.05
20	0.01344	0.1828	0.29082	5.1154	56.85
40	0.01602	0.2179	0.34666	5.19354	66.75
60	0.02067	0.2811	0.44728	5.2664	84.93
80	0.02303	0.3132	0.49835	5.33574	93.40
100	0.02668	0.3628	0.57733	5.4	106.91

CHAPTER 4

1. CONCLUSION

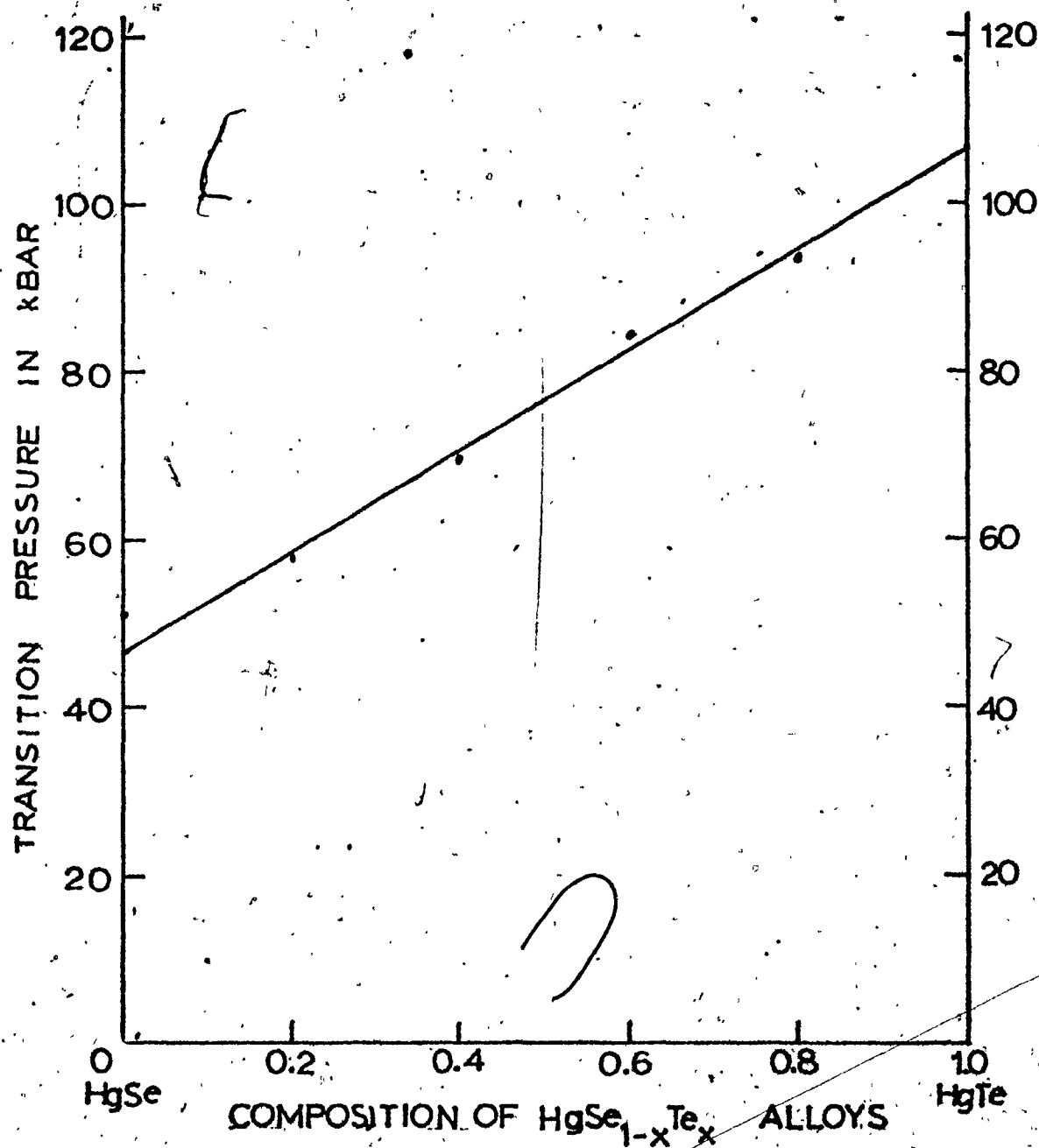
Though the equation developed contains a number of approximations and the result involves the difference of two energy terms which are a few hundred times larger than the difference, the linear dependence of transition pressure to nearest neighbors distance is clearly indicated. The calculated results are about seven times larger than the experimental value. However when the uncertainty of the energy terms is taken into consideration the results nevertheless are satisfactory. It is interesting to note that Jacobs' computed results are also larger than experimental results by about the same magnitude.

In fig. 4 Jacobs results for Rubidium and Potassium halides has been plotted. Figure 5 shows results for  $\text{HgSe}_{1-x}\text{Te}$  alloys. It can be seen that the slope of the  $\text{HgSe}_{1-x}\text{Te}$  alloys is positive whereas those of metallic halides are negative. This is attributed to the fact that the nearest neighbors distance for alkali halides increases at transition pressure whereas for mercury chalcogenides the nearest neighbors distance decreases at transition pressure.



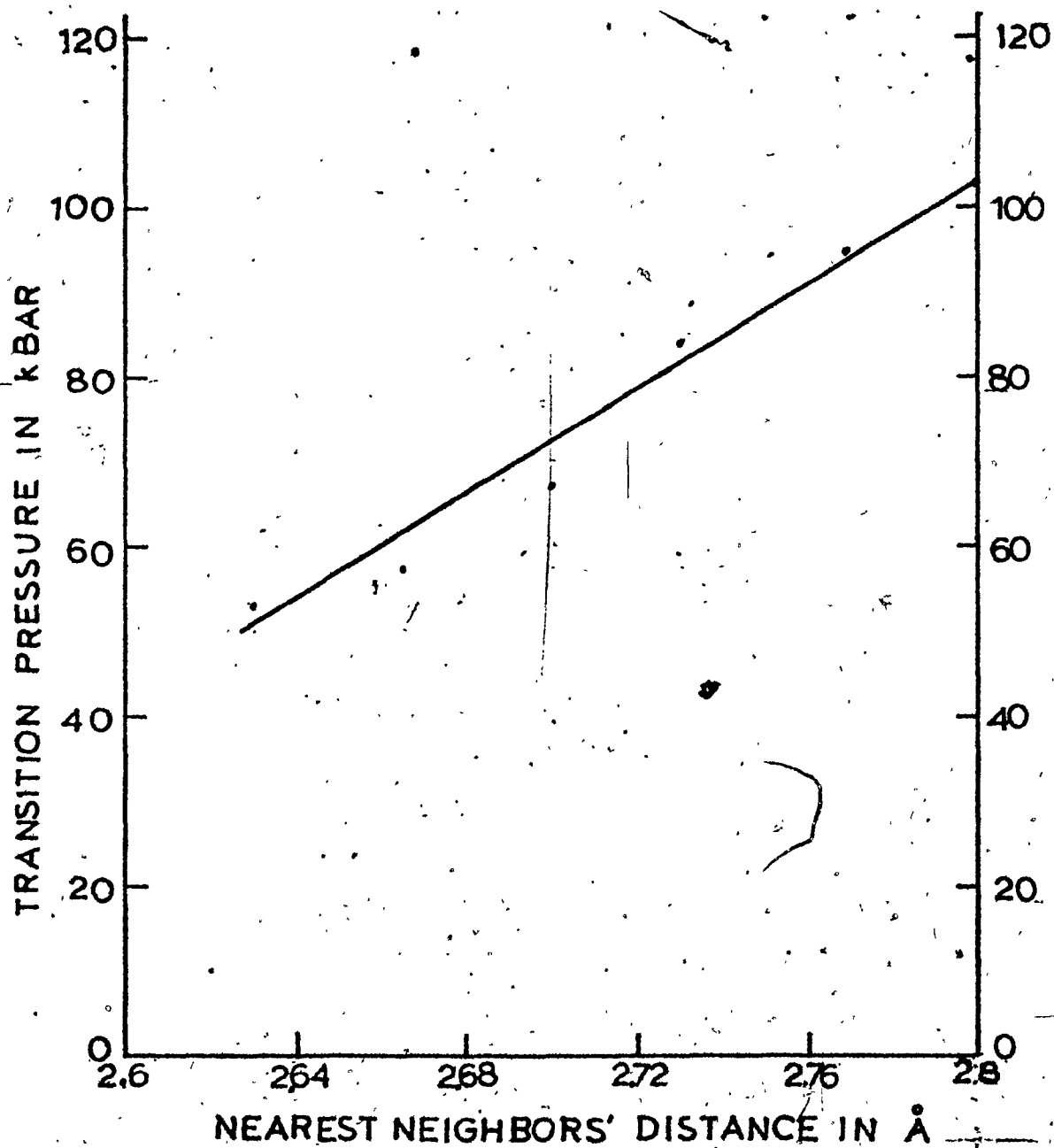
Interatomic Distance of  $\text{HgSe}_{1-x}\text{Te}_x$

FIGURE 1



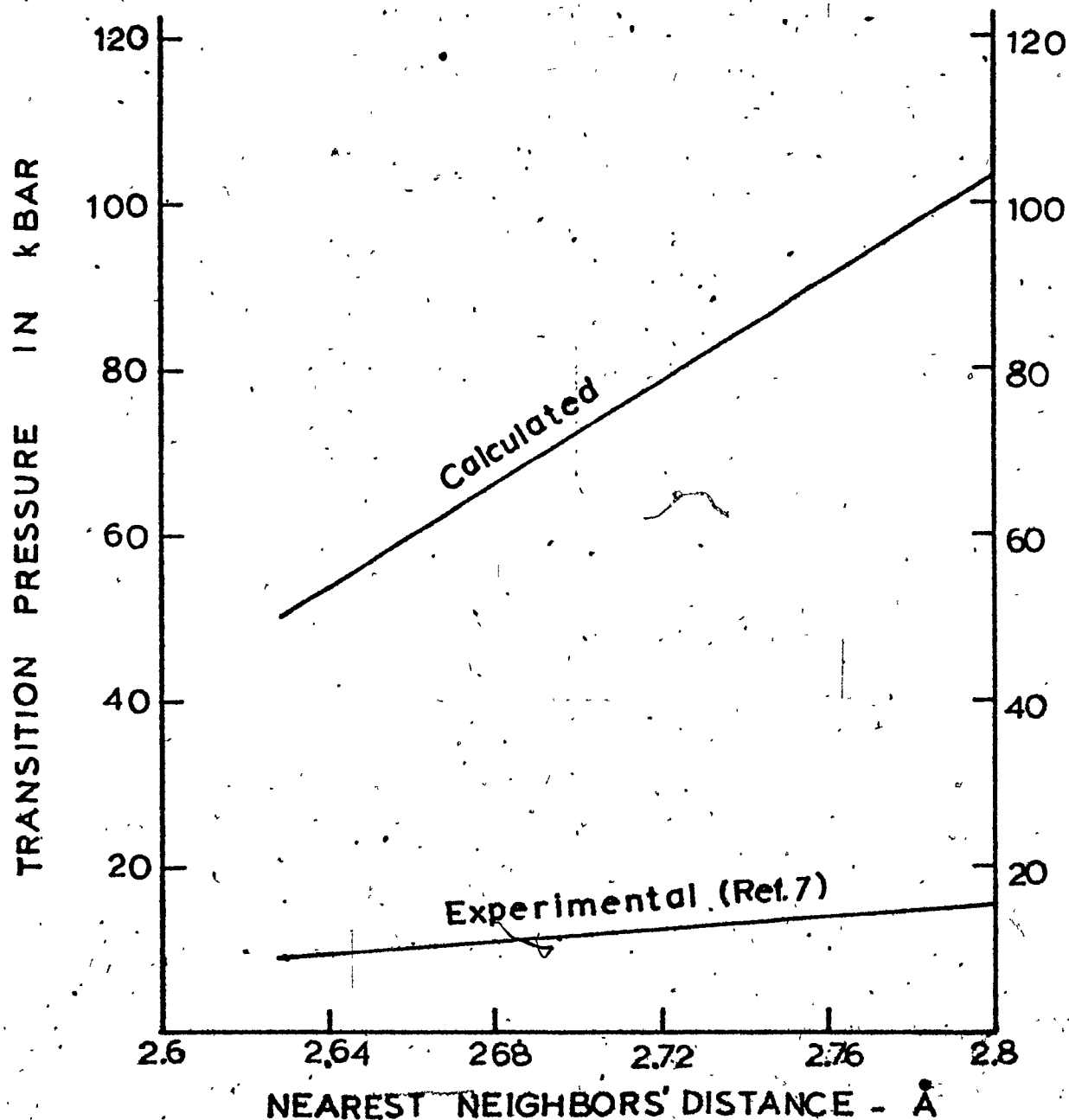
Calculated Transition Pressure as a  
Function of alloy Composition

FIGURE 2



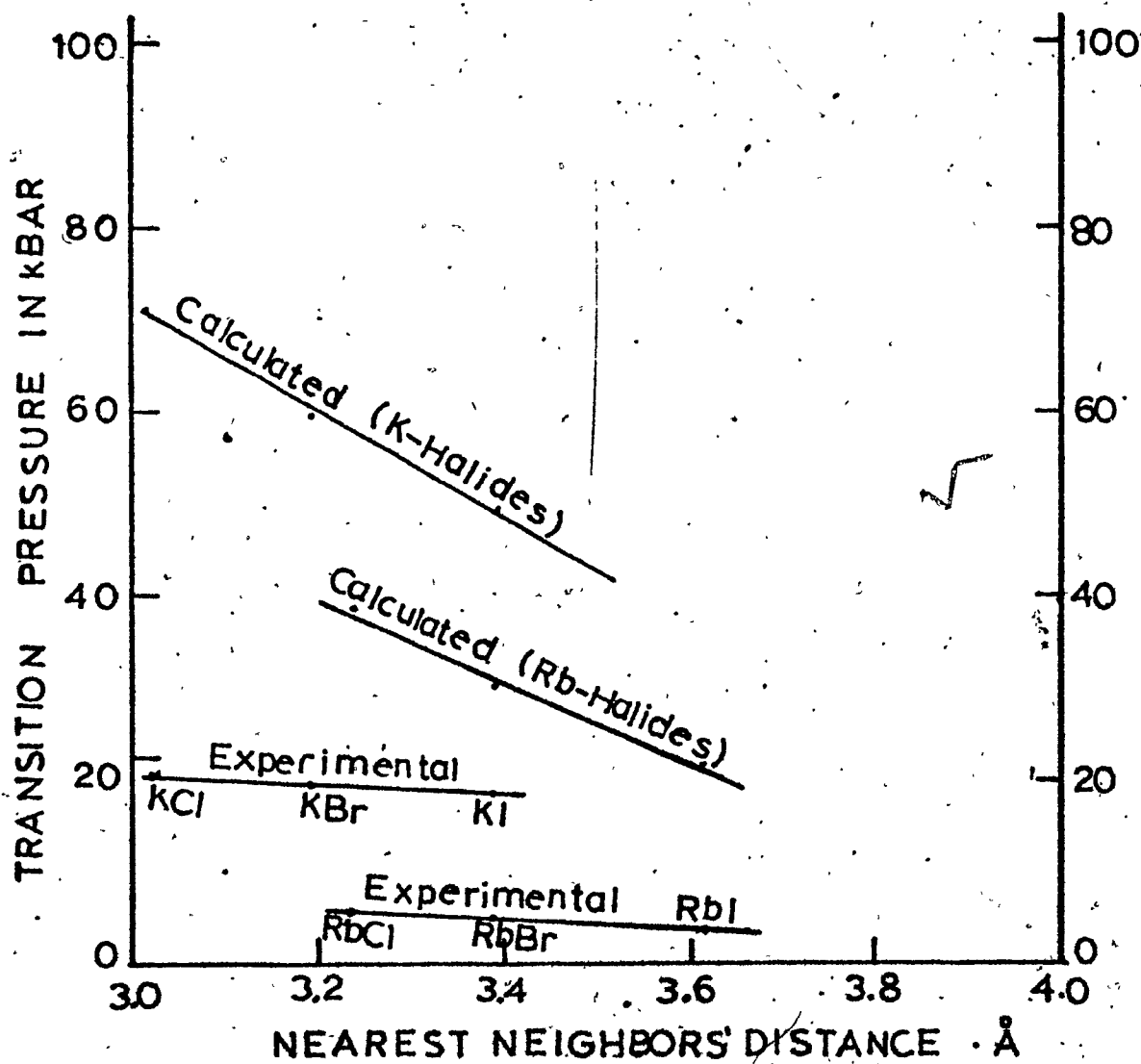
Transition Pressure as the Function of  
THE Nearest Neighbors' Distance

FIGURE 3



Comparison of calculated and  
Experimental Results of  
HgSe<sub>1-x</sub>Te<sub>x</sub> Alloys

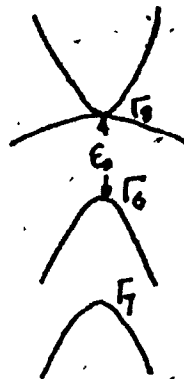
FIGURE 4



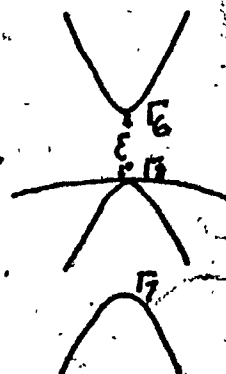
Comparison of Calculated and  
Experimental Results of Alkali  
Halides

FIGURE 5





Semi-metal Band Model



Semiconductor Band Model  
(Kane Model)

The Band Structure of  
Mercury Chalcogenides

FIGURE 6

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